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THE APPLICATION OF THERMOELECTRIC DEVICES AS SPACECRAFT THERMAL CONTROL COATINGS

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An elementary introduction to thermoelectric devices is given. The "figure of merit" and associated factors are subsequently discussed.

Theoretical calculations with bismuth telluride as a semiconductor model are exhibited, and a basic scheme for deposition of a thin-film array as a thermal control coating is presented. In addition, the thermal constraints of Skylab I are presented as a means of example for the utilization of active thin-film thermoelectric array devices.

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LIST OF SYMBOLS

Bi_2Te_3	-	Chemical Formula for Bismuth Telluride
TED	-	Abbreviation of Thermoelectric Device
Z	-	Figure of Merit, /Degree
α	-	Thermoelectric Power, Microvolt/Degree
α_p	-	p-type Thermoelectric Power, Microvolt/Degree
α_n	-	n-type Thermoelectric Power, Microvolt/Degree
k	-	Thermal Conductivity, Watt/Meter-Degree
k_p	-	p-type Thermal Conductivity, Watt/Meter-Degree
k_n	-	n-type Thermal Conductivity, Watt/Meter-Degree
γ	-	Resistivity, Ohm-Meter
γ_p	-	p-type Resistivity, Ohm-Meter
γ_n	-	n-type Resistivity, Ohm-Meter
T	-	Temperature, Degree
T_o	-	Cold Junction Temperature, Degree
T_h	-	Hot Junction Temperature, Degree
ΔT	-	Cold Junction Temperature - Hot Junction Temperature, Degree
A_n	-	Surface Area of Device n-type Material, $Meters^2$
A_p	-	Surface Area of Device p-type Material, $Meters^2$
L_n	-	Length of Device n-Leg, Meters
L_p	-	Length of Device p-Leg, Meters
[I]	-	Device Apparent Working Current, Amperes

LIST OF SYMBOLS (Concluded)

R	-	Device Resistance, Ohms
R_1	-	Load Resistance, Ohms
α_{pn}	-	Device Differential Thermoelectric Power, Microvolts/Degree
π_{pn}	-	Device Peltier Coefficient, Microvolts
C.O.P.	-	Coefficient of Performance

THE APPLICATION OF THERMOELECTRIC DEVICES AS SPACECRAFT ACTIVE THERMAL CONTROL COATINGS

SUMMARY

Calculations indicate that it is possible to optimize area and thickness ratio of thermoelectric devices so that they may be applied successfully as spacecraft thermal control coatings.

A favorable method of depositing thin-film arrays as a thermal control coating has been proposed, and the thermal constraints of Skylab I have been used as an example for utilization of thin film thermoelectric arrays.

INTRODUCTION

Basic Thermoelectric Device Theory

All known conventional spacecraft passive thermal control coatings are susceptible to inflight radiation damage and degradation by various contaminants. Passive coatings also offer no real versatile means of controlling cabin temperature. The use of thermoelectric devices is considered here as a means of alleviating these problems.

Thermoelectric devices are constructed by connecting n- and p-type semiconductor bar material through a good electrical conductor to form a single heat transfer element. In addition, these elements may be connected in series or parallel based upon the electrical and heat transfer factors of varied situations with the circuit ends in contact with some electrical energy source. As current flows through the entire device, the metal conductors will either heat or cool (due to summation of the Peltier, Seebeck, and Thomson effects), depending on the direction of direct current flow. A thermoelectric device operating in this manner is referred to as a thermoelectric heat pump.

In addition, opposite metal ends of thermoelectric devices may be exposed to a temperature gradient. When this condition exists, direct current will flow from one semiconductor bar material through an external circuit into the second bar material and the circuit will operate as a thermoelectric generator. These phenomena are the result of the summation of three thermoelectric parameters. First, the Peltier effect which states that as current is driven across the junction of two metals, the contact either heats or cools depending on the direction of current flow. The Thomson effect which states that when different parts of the same metallic conductor are maintained at different temperatures, a potential difference may be observed in the conductor. Finally, the Seebeck effect which says that if two wires of disimilar metal are joined at their ends, and these ends are maintained at different temperatures, a current may be observed in the wires of the circuit.

The above mentioned phenomena, associated with thermoelectric devices, can be utilized in a thermal control coating for spacecrafts. The desired features of such a reversible device would also include a thin coating providing a surface that is not damaged by radiation and a versatile means of controlling cabin temperatures as desired by the occupants.

In order to obtain maximum benefit from such individual semiconductor devices, they would have to be developed as large thin-film, lightweight arrays of semiconductor material, have low extraneous power requirements, and be economically feasible to apply to a variety of structural geometries. A pictorial example of an elementary thermoelectric device is shown in Figure 1.

Figure of Merit

It may be deduced from Figure 1 that the most important component of a thermoelectric device is the semiconductor materials. Selection of the semiconductor material is based upon a term called "figure of merit," denoted by the letter Z. This property is specific for every semiconductor compound. The value of the "figure of merit" is given by the following equation:

$$Z = \frac{\alpha^2}{k\gamma} \qquad (1)$$

where:

Z = Figure of merit (/Deg)
α = Thermoelectric power (μV/Deg)
k = Thermal conductivity (Watt $M^{-1} Deg^{-1}$)
γ = Resistivity (Ohm-M)

When two semiconductor compounds are involved in a thermoelectric device, the overall "figure of merit" for the device is given by the following equation:

$$Z = \frac{(\alpha_p - \alpha_n)^2}{(\sqrt{k_p\gamma_p} + \sqrt{k_n\gamma_n})^2} \tag{2}$$

Higher quality thermoelectric devices will be derived from semiconductor compounds with greater Z values.

Examination of the "figure of merit" equation indicates that Z may be improved by either increasing thermoelectric power or by decreasing k and γ. Since thermoelectric power, or the Seebeck coefficient, is basically a function of the Fermi level of the original material, no attempt is made to alter α. Generally, Z values of a semiconductor material are improved by lowering either k or γ, or both. Insight into the effect of reducing k and γ can be derived from the Weidemann-Franz ratio which is given here in a generalized form by the equation:

$$k\gamma = cT \tag{3}$$

where:

k = Thermal conductivity
γ = Resistivity
c = Constant
T = Temperature

It is apparent that when γ has been optimized, k has been minimized. However, it has been found that by suitably doping semiconductor compounds, k can be lowered by as much as 50 percent while γ remains approximately constant. The reason generally advanced in explaining this phenomenon is that the impurity atom interatomic distance is closer to phonon wave lengths than carrier wave lengths.

Another method of reducing k while γ remains constant is by alloying dissimilar semiconductor compounds. Increasing composition in one direction for certain compounds lowers the lattice thermal conductivity while the original resistivity remains approximately constant. At present, there is no theoretical explanation for this phenomenon.

Based upon present day technology, it has been found that bismuth telluride (Bi_2Te_3) compounds, when suitably doped, offer maximum "figure of merit." Many of these compounds exhibit Z values as high as 3×10^{-3} deg^{-1} (3).

CALCULATIONS CONCERNING THERMOELECTRIC DEVICES

Area Optimization by Using Fundamental Electrical Properties Data for Bi_2Te_3

The cross sectional area ratio of the type of semiconductor bar material used in these thermoelectric devices may be calculated from the following equation:

$$\frac{A_n}{A_p} = \frac{\gamma_n B + \sqrt{(\gamma_n/\gamma_p)\ [1 + B(\gamma_n/\gamma_p)]}}{1 - B\gamma_p} \qquad (4)$$

where:

$\frac{A_n}{A_p}$ = Area ratio of n material to p material

γ = Resistivity

B = A mathematical condensation constant which directly relates thermal conductivity and thermoelectric power difference ratio with temperature.

An expression for B is as follows:

$$B \doteq \frac{2(k_p - k_n)\,\Delta T}{(\alpha_{pn})^2 T_h^{\ 2}} \qquad (5)$$

where:

k = Thermal conductivity
α_{pn} = $(\alpha_p - \alpha_n)$
T_h = Hot side temperature
ΔT = Cold junction temperature - hot junction temperature

Assuming a T_h of approximately 300°C and a ΔT of -279°C, for certain bismuth telluride alloys, B is obtained, using given parameter values (4) by the following relations:

$$\alpha_p = 280$$

$$\alpha_n = 185$$

$$k_p = 3.10 \times 10^{-3}$$

$$k_n = 2.0$$

$$B = \frac{2(3.10 \times 10^{-3} - 2.0)(-279)}{(280 - 185)^2 \ (300)^2} \tag{6}$$

$$B = 1.37 \times 10^{-6}$$

By substituting the proper numerical values in equation (4), we obtain the area ratio distribution for n and p type semiconductors:

$$\frac{A_n}{A_p} = \frac{\gamma_n(1.37 \times 10^{-6}) + \sqrt{(\gamma_n/\gamma_p) \ [1 + (1.37 \times 10^{-6}) \ (\gamma_n/\gamma_p)]}}{1 - (1.37 \times 10^{-6})\gamma_p} \tag{7}$$

for bismuth telluride alloy, γ_n and γ_p are:

$$\gamma_n = \frac{1}{850} \text{ ohm cm}^{+1} = 0.0012\,\Omega \text{ cm}^{+1}$$

$$\gamma_p = \frac{1}{85.79} \text{ ohm cm}^{+1} = 0.0116\,\Omega \text{ cm}^{+1}$$

therefore:

$$\frac{A_n}{A_p} = \frac{(1.2 \times 10^{-3})(1.37 \times 10^{-6}) + \sqrt{\left(\frac{1.2 \times 10^{-3}}{1.16 \times 10^{-2}}\right)\left[1 + (1.37 \times 10^{-6})\left(\frac{1.2 \times 10^{-3}}{1.16 \times 10^{-2}}\right)\right]}}{1 - (1.37 \times 10^{-6})(0.0116)} \quad (8)$$

$$\frac{A_n}{A_p} = \frac{0.322}{1} \cong \frac{1}{3}$$

The actual area of a semiconductor leg is not randomly selected but must consider both the thickness and length of the material. Area thickness ratios are calculated from the following equation:

$$\left(\frac{A_p L_n}{A_n L_p}\right)^2 = \left(\frac{\gamma_p k_n}{\gamma_n k_p}\right) \quad (9)$$

where A and L are area and length, respectively, and other terms are defined above

$$\left(\frac{A_p L_n}{A_n L_p}\right)^2 = \frac{0.0116 \times 2.0}{0.0012 \times 3.10 \times 10^{-3}} \quad (10)$$

$$\left(\frac{A_p L_n}{A_n L_p}\right)^2 = 0.6236 \times 10^{+4}$$

$$\frac{A_p}{A_n} \frac{L_n}{L_p} = 7.89 \times 10^1$$

$$\frac{A_p}{A_n} = \frac{1}{0.322} \quad \text{from previous calculation}$$

thus,

$$\frac{L_n}{L_p} = 25.40$$

Upon assuming A_p/L_p = 100,000 for p-type bismuth telluride, the area to length ratio for n-type bismuth telluride is:

$$\frac{A_n}{L_n} = 1.267 \times 10^{+3} \tag{11}$$

Optimized surface area with respect to thickness of a thin film array of properly doped thermoelectric (Bi_2Te_3) devices operating under a hot temperature of 300°C with a ΔT of -279°C across the device is presented in Table I.

TABLE I

B	T	L_n/L_p	A_p/A_n	A_p/L_p	A_n/L_n
1.37×10^{-6}	-279°C	25.40	3.11	100,000	$1.267 \times 10^{+3}$

APPARENT CURRENT PRODUCED BY AREA OPTIMIZED Bi_2Te_3 DEVICES

The maximum current produced by this optimized device functioning as a generator on the cold side is given by (5):

$$[I] = \alpha_{pn} \left[\frac{T_o - T_1}{R_1 + R} \right] \tag{12}$$

where: $[I]$ = Apparent current

$T_o - T_1$ = Cold junction temperature - hot junction temperature = ΔT.

Assuming that the surface areas of both devices are equal,

$$[I] = \alpha_{pn} \left[\frac{T_o - T_1}{2R}\right] \tag{13}$$

where:

$$2R = 2\left(\gamma_p \frac{L_p}{A_p} + \gamma_n \frac{L_n}{A_n}\right) \tag{14}$$

Stipulating

$$\frac{L_p}{A_p} = 1 \times 10^{-5}, \quad \frac{L_n}{A_n} = 7.89 \times 10^{-4}$$

$$2R = 2(0.0116 \times 10^{-5} + 0.0012 \times 7.89 \times 10^{-4})$$

$$2R = 2(1.16 \times 10^{-7} + 9.46 \times 10^{-7})$$

$$2R = 2(10.62 \times 10^{-7})$$

$$2R = 21.24 \times 10^{-7}$$

$$R = 10.62 \times 10^{-7}$$

$$[I] = \alpha_{pn} \frac{(T_o - T_1)}{2R}$$

$$\alpha_{pn} = 95 \ \mu v/deg = 95 \times 10^{-6} \ v/deg$$

$$[I] = \frac{95 \times 10^{-6} \times (-279)}{21.24 \times 10^{-7}}$$

$$[I] = -12{,}478.8 \text{ amps}$$

$$[I] = 12{,}478.8 \text{ amps}$$

where:

[I] = apparent working current assuming a C.O.P. of unity and complete utilization of cold side surface area.

If a cabin temperature is to be maintained at say 21°C, the question arises as to what will be the controllable hot side temperature if thermoelectric generators on the cold side are used to drive the hot side thermoelectric heat pump. This question may be resolved by examining the following equation:

$$[I] = \pi_{pn}/R \tag{15}$$

where,

$$\pi_{pn} = T_h (\alpha_p - \alpha_n)$$

and,

$$T_h = \text{hot side surface temperature.}$$

thus, substituting the proper relation for π_{pn} we see that

$$[I] = T_h (\alpha_p - \alpha_n)/R$$

solving for the term T_h,

$$T_h = \frac{[I] \times R}{\alpha_p - \alpha_n}$$

$$T_h = \frac{12{,}478.8 \times 10.62 \times 10^{-7}}{95 \times 10^{-6}}$$

$$T_h = 139.5°C$$

THE USE OF THERMOELECTRIC COOLING DEVICES INVOLVING SURFACE AREA

If one considered a thermal control problem involving Skylab I, using surface area parameters as shown in Table II, an effective control array could be designed to precisely regulate and transfer surface absorbed radiation.

TABLE II

Total Surface Area	3,000 ft^2
Average Cold Surface Area	0.60 x 3,000 = 1,800 ft^2
Average Hot Surface Area	3,000 - 1,800 = 1,200 ft^2

Since surface areas of the generator and the refrigerator were assumed to be equal in previous calculations to determine T_h, the calculated generator output would be effected by changes in the surface area ratio. This new output could be calculated from the following expression:

$$[I] = [I_1] \times \frac{\text{Surface Area Generator}}{\text{Surface Area Refrigerator}}$$

$[I_1]$ = 12,478.8 amps, from previous calculations

$$\frac{1{,}800}{1{,}200} = \frac{\text{Surface Area Generator}}{\text{Surface Area Refrigerator}} \quad \text{ratio for Skylab L}$$

$[I]$ = 12,478.8 x 1.5

$[I]$ = 18,718.2 amps

This produced current, [I], again is calculated using a device C.O.P. of unity and assuming complete utilization of cold side surface area.

A calculation for T_h based upon Skylab geometric parameters is as follows:

$$T_h = \frac{[I] \times R}{\alpha_p - \alpha_n}$$

$$T_h = \frac{18,718.2 \times 10.62 \times 10^{-7}}{95 \times 10^{-6}}$$

$$T_h = 209.25°C$$

A means of circumventing this seemingly low T_h (compared to the expected T_h of 300°C) would be to alternately cool areas on the hot side. Areas on the hot side could be alternately cooled and generators could be converted to heat pumps and vice versa through electronic switching circuits. These switching circuits would consist of nothing more than thermocouples imbedded in specific regions of devices and solid state solenoid-operated current directors. Therefore, it is possible that by using thin film thermoelectric array devices the power now required to operate the overall environmental control system in a Skylab system can be radically reduced.

INSTALLATION OF THIN-FILM THERMOELECTRIC DEVICE ARRAY

Actual installation of thermoelectric devices as a thermal control coating could be accomplished by depositing thin film array of metal and semiconductor material on a mechanically attachable surface, or by deposition intimately on the spacecraft surface.

Basically, there are two favorable methods of transporting semiconductor material from a bulk source to a deposition surface. These methods are the flash evaporation process and the close-spaced method.

In the flash evaporation method, individual grains of semiconductor material are contacted with a surface temperature sufficiently high to immediately sublimate the material. Compound stoichiometry in the deposition surface is presently somewhat difficult to control because substrate temperature must be maintained relative to the material source temperature.

A temperature gradient between the source and substrate is also necessary in the close-spaced method. However, if the spacing is about 1/10 of the diameter of the source and substrate, then the chemical transport conditions are independent of the conditions elsewhere in the system. Transport agents such as oxygen are not consumed in this process and are available for re-use as transport agents between source and substrate. This process is particularily well suited for covering large areas with semiconductor deposits.

Doping can be carried out by transport from the source material or by adding a suitable dopant as a vapor during the growth of the layer. Regardless of the final deposition surface, the deposition process could theoretically be carried out in the four pictorial steps shown in Figure 2.

RESULTS OF APPLICATION OF THERMOELECTRIC DEVICES AS THERMAL CONTROL COATINGS

Specific Characteristics of Coatings

The thin film array to be finally employed as a thermal control coating for spacecraft should be a film of about 12 mils thick which will have an add-on weight of about one pound per square yard compared to S-13G which has an add-on weight of roughly 0.8 pound per square yard of coating surface area.

Efficiency of the device will be at least 25 percent improved by using a thickness optimized film which will show considerable improvement in radiation damage resistance.

This thermal control coating concept could offer space travelers the first real versatile means of controlling spacecraft surface temperatures regardless of the orbital altitudes.

Problems Associated with Thermoelectric Devices as Thermal Control Coatings

The operation of thermoelectric devices as a heat pump must be started initially with an extraneous power source, otherwise the heat pumps would act as a generator regardless of the direction of temperature gradient. The heat pump could be started by energy provided by either a disposable or on-board power source.

Experimental work must progress in devising means of controlling the thermal conductivity of the semiconductor device. The thermal conductivity of semiconductors approach that of asbestos by a factor of fifteen as a thermal insulator.

CONCLUSIONS

It has been demonstrated theoretically that certain thermoelectric devices may be used as thermal control coatings. However, research in several areas is required before this technique can provide an economically competitive system to the passive coatings presently used.

Attempts will be made to improve the "figure of merit," Z, for existing best known materials. Deposition techniques are to be developed and scale vehicle environmental tests will be done to evaluate the effectiveness of this thermal control concept.

Service life coupled with true ability to control cabin temperature will eventually be assessed. However, basic Thermoelectric device theory provides confidence and proof of validity even though the major engineering problems remain to be solved.

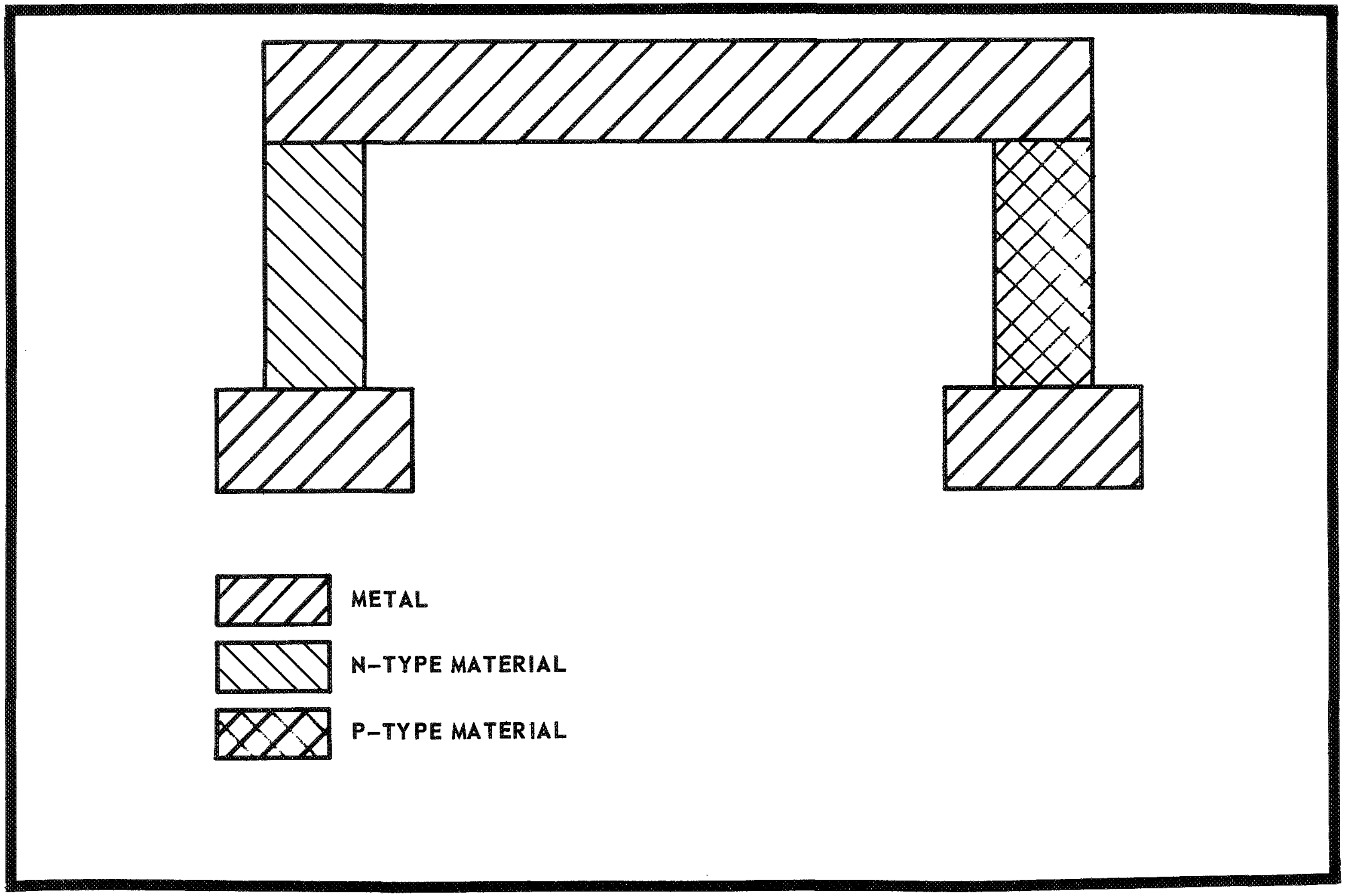


FIGURE 1 PICTORIAL EXAMPLE OF AN ELEMENTRY THERMOELECTRIC DEVICE

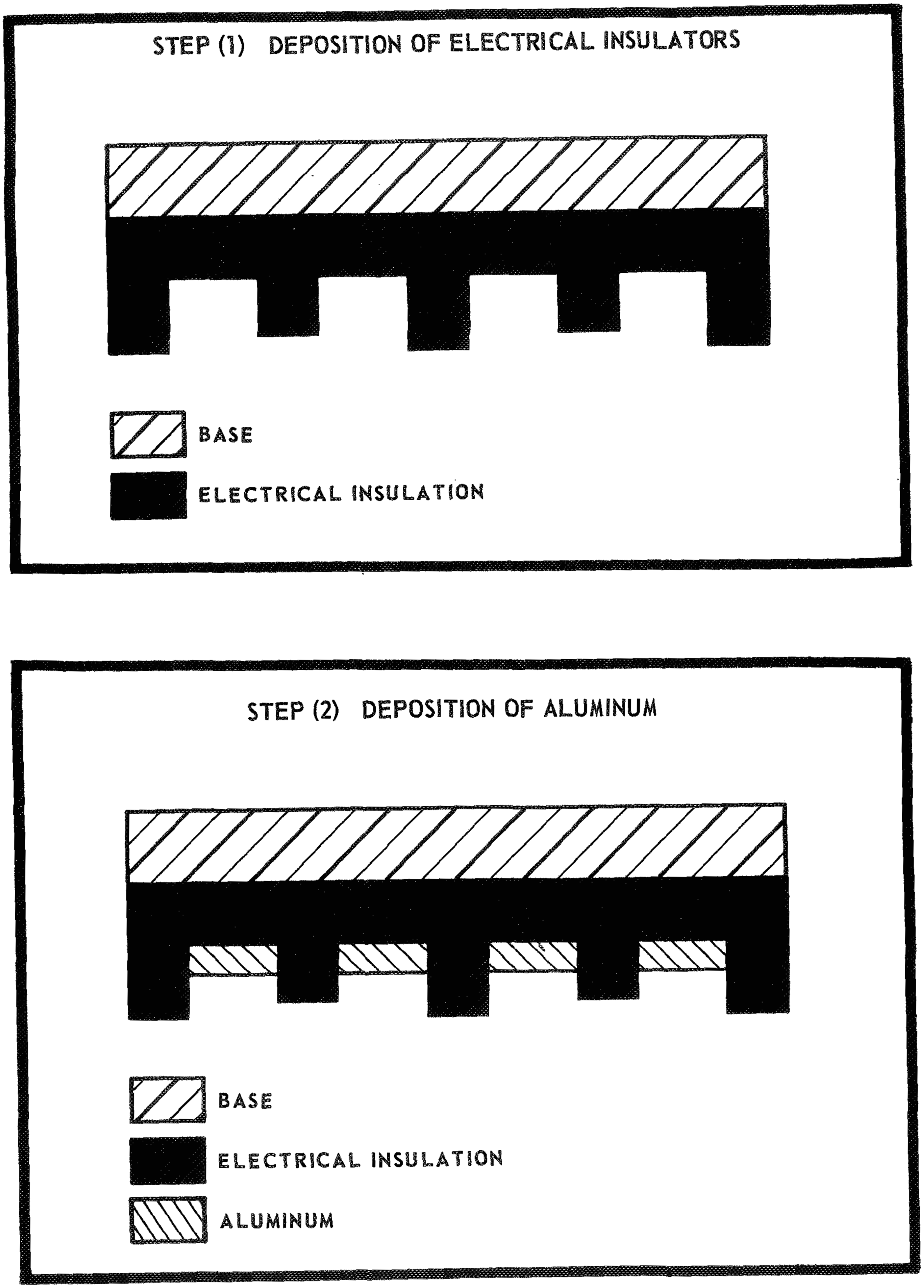
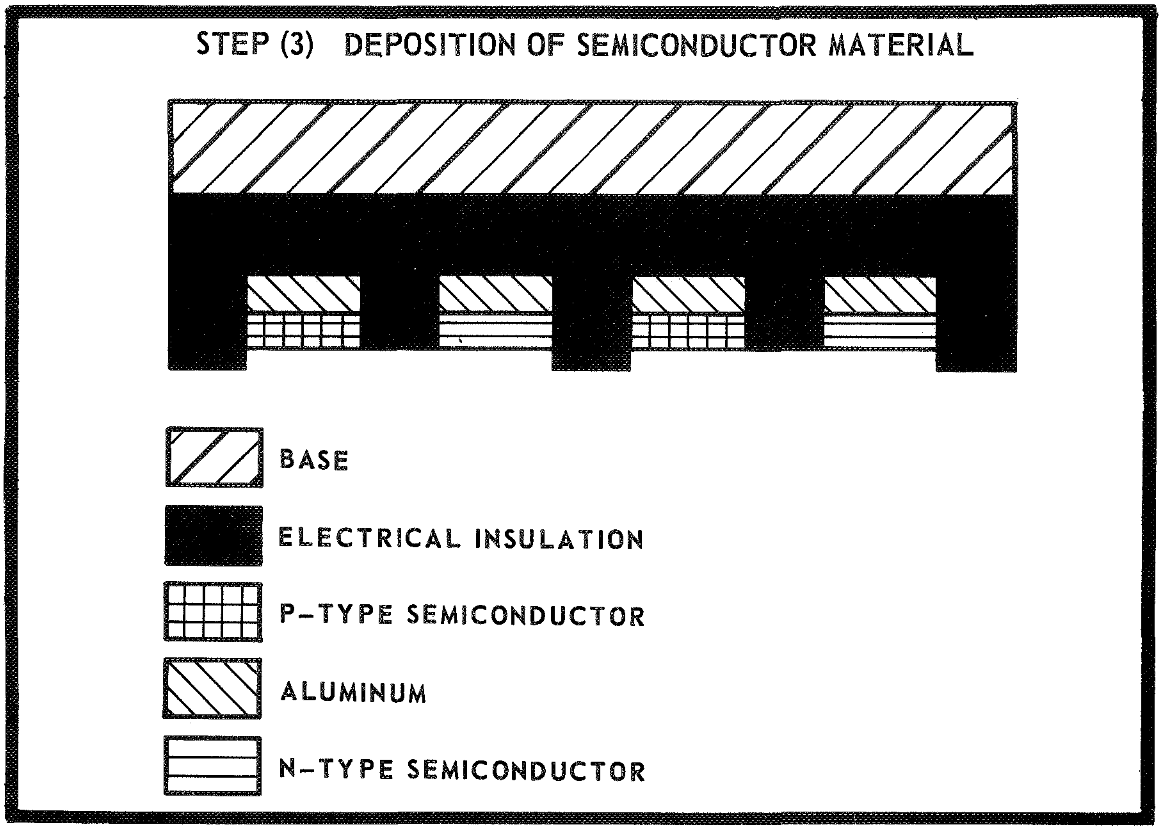


FIGURE 2. FABRICATION OF A THIN-FILM THERMOELECTRIC DEVICE



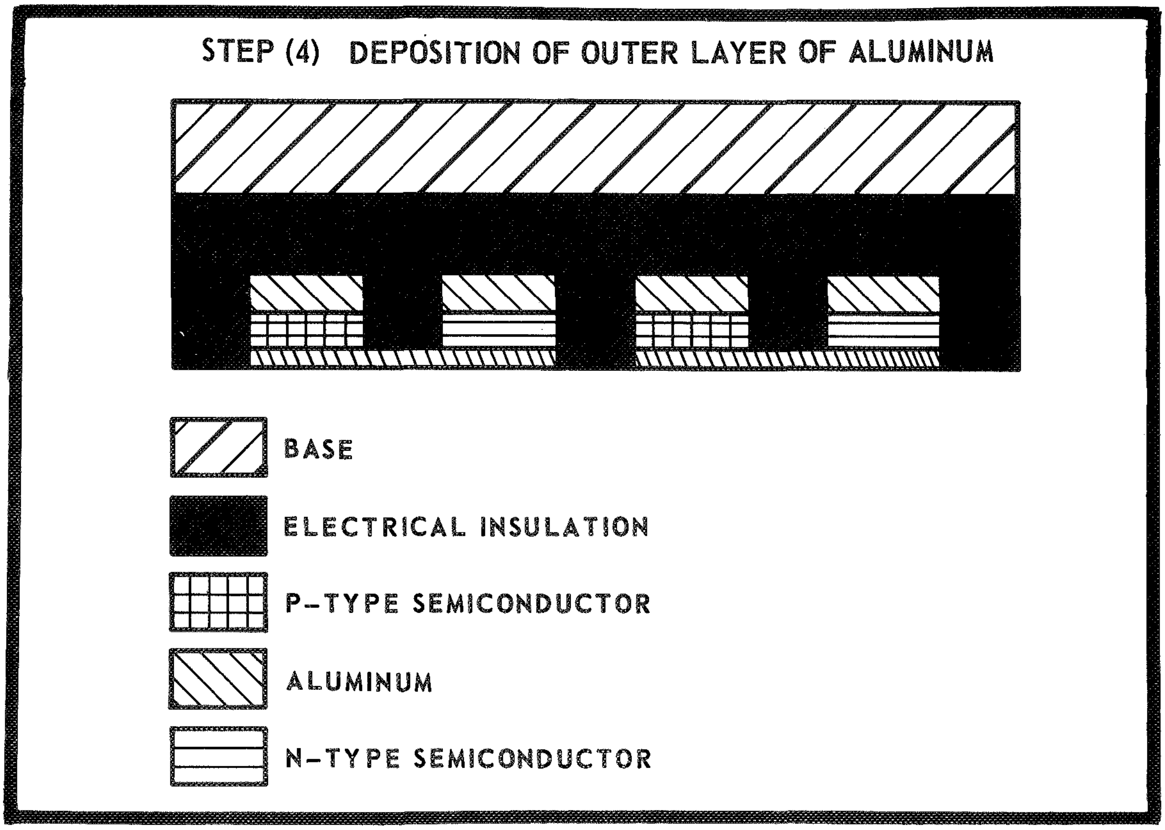


FIGURE 2. FABRICATION OF A THIN-FILM THERMOELECTRIC DEVICE(Concluded)

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This document has also been reviewed and approved for technical accuracy.

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